

Surface Chemical Transformations of UV Irradiated Silica-Epoxy Nanocomposites

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ABSTRACT

Silica nanocomposites (SiNCs), which are silica nanoparticles (SiNPs) incorporated into a polymeric matrix, are used in a wide variety of commercially available products for numerous applications. Environmental factors, such as light, may modify the SiNCs during their lifetime of service, giving rise to the possibility of degradation leading to SiNP release. Ultimately, light-induced modifications are most likely to occur at the SiNC-air interface, which suggests that surface transformations will play a major role in the potential release of SiNPs throughout the lifecycle of this material. To better understand these surface transformations, we investigated the impact of high intensity simulated solar radiation (290 nm to 400 nm) on the surface and bulk properties of SiNCs created from unmodified SiNPs. Surface spectroscopic analysis (XPS) was employed to understand the chemical transformations that occur as a result of UV-aging of SiNCs. Results demonstrate that UV-induced transformations of SiNCs occurred via photo-oxidation of the epoxy matrix resulting in a subsequent loss of polymeric material and surface enhancements in the silicon and nitrogen concentrations.

Keywords: silica, nanoparticles, nanoEHS, photodegradation, nanocomposites, surface analysis

1. INTRODUCTION

The incorporation of nanomaterials into matrices or supports to form composite materials has been of growing interest to both academic and industrial research community. These nanocomposites are of interest due to the new or improved properties that they may possess upon incorporating nanoscale materials (<100 nm). These nanocomposites include two components: the matrix material, which makes up the majority of the composite, may be composed of a metal, ceramic or polymer; and one or more nanomaterials, which can include carbon nanotubes, nanoscale metal oxides and/or silica nanoparticles (SiNP) [1]. The current study focuses on the use of SiNPs that have been incorporated into a polymeric matrix consisting of an epoxy.

Incorporation of SiNPs into composites, or silica nanocomposites (SiNCs), has become an important component of many products due to their enhanced mechanical strength and chemical resistance [1, 2]. However, with the growing interest in the use of these

novel materials, there is also a growing concern about the impact of these materials on the environment during their use and after their service life. Some of these concerns can manifest via chemical transformations and nanoparticle release. Among these concerns is the need to better understand transformations caused by the local environments of nanomaterial containing products, such as nanocomposites, over their complete life cycle [3, 4]. The surface of the SiNCs, however, is likely to be the location of the initial transformations making understanding surface properties key to elucidating issues during the service life.

One factor that may influence the SiNC surface is the presence or absence of sunlight. Ultraviolet (UV) light, which has the highest energy component of sunlight, is most likely to react with the surface. NIST is ideally suited to investigate the effects of light on SiNCs due to the presence of instrumentation such as the SPHERE (Simulated Photodegradation via High Energy Radiant Emission), which exposes composites to high fluxes of light representative of the UV component of solar radiation [5].

The focus of this study will be to understand the chemical transformations occurring at the surface of model SiNCs with increasing simulated solar exposure. To gain this understanding, X-ray photoelectron spectroscopy (XPS) was employed to analyze the surface and near surface transformations. Additionally, the effect of varying the characteristics and surface chemistry of the SiNPs was compared and contrasted to SiNCs studied in previous studies.

2. MATERIALS AND METHODS¹

2.1 Sample preparation

General sample preparations for SiNCs consisting of epoxy and SiNPs can be readily found in the literature [6, 7]. Briefly, the 2-part epoxy component of the composite consisted of diglycidal ether of bisphenol A (DGEBA) resin (Epon 828, Resolution Performance Products) and a curing agent (Jeffamine T403, Huntsman Corporation, Woodlands, TX). 15 nm SiNPs (Aldrich, St. Louis, MO) that had clean,

¹ Certain trade names and company products are mentioned in the text or identified in illustrations in order to adequately specify the experimental procedure and equipment used. In no case does such identification imply recommendation or endorsement by National Institute of Standards and Technology, nor does it imply that the products are necessarily the best available for the purpose.

unmodified surfaces were mixed into the 2-part epoxy to achieve a 5 % silica concentration by mass (dry weight). The combined SiNP and epoxy components were mixed together via magnetic stirring and sonication in attempts to achieve a homogenous mixture. The mixture was then drawn down, dried and cured into the final SiNC. The SiNC was then cut to an appropriate size prior to use.

2.2 UV exposure

UV exposure of the cured SiNCs took place on the NIST SPHERE in 17 specimen sample holders that have been described elsewhere [8]. It is important to note that when the samples were UV exposed, they were kept within temperature and humidity controlled chambers. Specifically, these samples were kept at 60 ° C and ≈ 0 % relative humidity. Samples were typically exposed for a prescribed period of time ranging between 0 days and 59 days, at which point the samples were removed, a select specimen was taken and the remaining samples were returned to the SPHERE for further UV irradiation.

2.3 X-ray photoelectron spectroscopy

XPS was performed on a Kratos Axis Ultra DLD (Kratos Analytical, Chestnut Ridge, NY) using monochromatic Al K α X-rays under system conditions previously described in other publications [8, 9]. The spectra acquired were at pass energies of 160 eV (survey, low resolution) and 40 eV (multiplex, high resolution). All spectra were charge neutralized in order to account for the insulating properties of the material. The high resolution spectra were energy corrected to adjust the C (1s) peak maximum to 284.5 eV for the hydrocarbon components as is comparable with previous studies [8, 10]. Atomic percentages were calculated using CasaXPS (Teignmouth, UK) for high resolution C (1s), O (1s), N (1s) and Si (2p) regions fit with Shirley baseline and adjusted using sensitivity factors of 0.278, 0.78, 0.477 and 0.328, respectively. All reported atomic percentages are based on the average ± 1 standard deviation of 3 separate measurements at high resolution.

3. RESULTS AND DISCUSSION

3.1 Visually observed changes

Visual observations revealed that the SiNCs were white/translucent prior to UV exposure, as demonstrated in Figure 1 (see left sample). The original samples were relatively hard and somewhat brittle. When exposed for 59 days to UV light, clear evidence of photodegradation could be observed on the surface of the SiNC, as demonstrated by the change in color from white/translucent to dark yellow/brown (Figure 1, right sample). This is consistent with previous research that reported the discoloration of SiNCs after prolonged UV exposure [8]. Furthermore, like

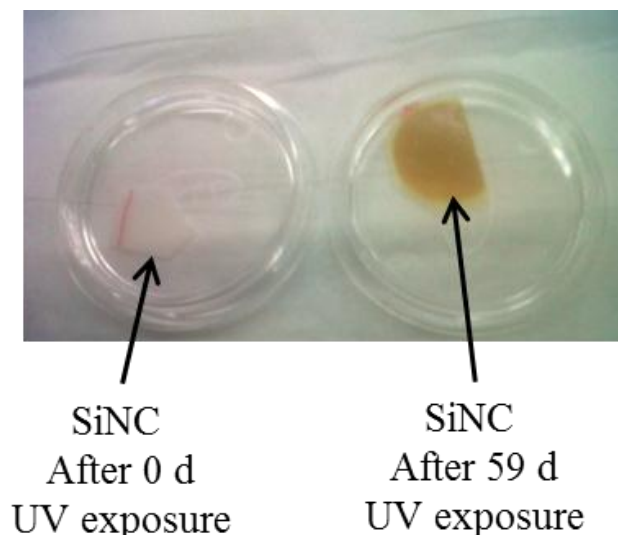


Figure 1: Picture of SiNCs before (left) and after (right) 59 days of simulated solar degradation. UV exposure causes visual transformations to the surface of the SiNCs from a white/translucent color to dark yellow/brown. Both samples are marked (red) to note the correct orientation.

previous studies, the SiNC became even more brittle at long exposures and much easier to crack or even break.

3.2 Elemental and Chemical Transformations

XP spectra were acquired to assess the transformative effects of UV light on the SiNCs by observing them before and after irradiation. Figure 2 illustrates the transformations that occurred to the elemental distributions over the course of 59 days. At day 0, the survey spectra were dominated by the C (1s) and O (1s) photoelectron peaks with trace amounts of N (1s) at approximately 284.5 eV, 533.5 eV and 399 eV, respectively, representative of all of the elements present in the epoxy. There was also a trace presence of the Si (2p) at approximately 102 eV. After 59 days of UV exposure, the O (1s) peak became even larger while the C (1s) peak diminished. Additionally, both the N (1s) and Si (2p) photoelectron peaks increased significantly.

To provide quantitative elemental transformations as well as chemical information, high resolution XP spectra were also acquired (Figure 3). The O, N, C and Si contributions at day 0 were measured at (17.7 ± 0.8) %, (1.4 ± 0.2) %, (77.4 ± 1.4) %, and (3.4 ± 0.8) %, respectively. Upon exposure to the UV light, the C (1s) surface composition decreased to (50.2 ± 1.7) % while the O (1s) and Si (2p) increased to (35.2 ± 1.6) % and (6.5 ± 0.4) %, respectively. This observation is consistent with the previously observed photodegradation via an oxidation of the epoxy based components, correspondingly increasing the surface concentration of SiNPs [8]. In contrast to this study, however, the N (1s) signal appears to also increase to (8.1 ± 0.2) % whereas previously these composites were

observed to remain at constant N (1s) photoelectron counts [8].

Further support of a mechanism dominated by photo-oxidation can be observed from the C (1s) spectra in Figure 3 (Upper left). The typical C (1s) spectra observed from a clean, unexposed surface dominated by hydrocarbon (CH/CC) at ≈ 284.5 and carbon bound to nitrogen or oxygen (C-O/C-N) with trace amounts of highly oxidized carbon (COO/CON) transforms dramatically by losing roughly half of the photoelectron intensity for the CH/CC and C-O/CN peaks while the highly oxidized carbon feature becomes a major component of the spectrum. The growth of the O (1s) peak corresponds well with the significant increase in the COO/CON component.

The high resolution spectra also suggest that photo-oxidation of the composite results in the removal of the epoxy/polymeric component with an increase in the SiNP surface concentration. An interesting finding is that the N (1s) spectra also exhibits an increase after long term exposure to UV radiation, a finding much different than previous studies [7, 8]. While it is currently unclear why this difference is observed, the use of clean, unsilanized

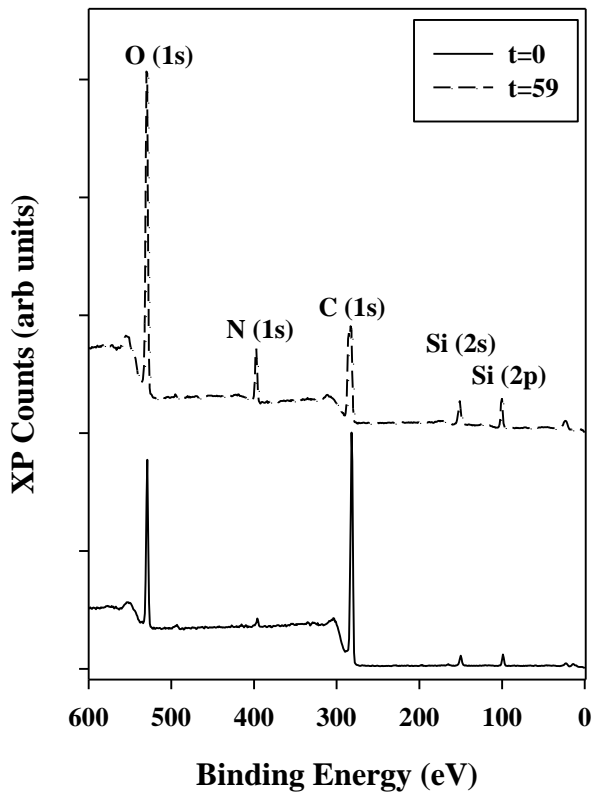


Figure 2: Low resolution, wide range XPS survey spectra of SiNCs exposed to 0 days (bottom) and 59 days (top) of simulated solar radiation. Analysis revealed that 59 days of exposure to UV light increased the O (1s), N (1s) and Si (2p) photoelectron counts while the C (1s) overall intensity appeared to decrease in intensity.

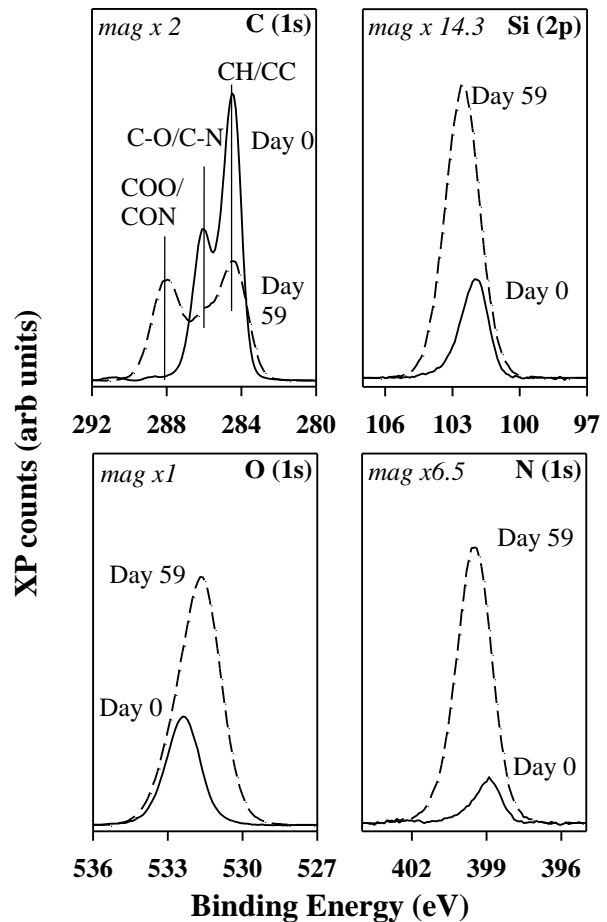


Figure 3: Representative, high resolution XP spectra of the SiNCs before and after 59 days of UV exposure for all of the elements observed within the high resolution scan. As in the survey scans, the solid lines are representative of Day 0 and the dashed lines are for Day 59. Magnifications relative to each other are provided.

SiNPs may preferentially adsorb the epoxy's high electronegativity nitrogen functionalities from the amine curing agent during processing and the subsequent removal of the carbonaceous component at the surface of the SiNC by photodegradation.

CONCLUSION

The surface transformations of SiNCs have been presented. SiNCs exposed to long term UV exposure ultimately undergo surface chemical transformations by way of photo-oxidation of the epoxy matrix. Contrary to silane stabilized SiNPs within a composite which did not show a change in the nitrogen percentage after photo-oxidation, incorporation of the 'clean' SiNP into the SiNC results in an increased atomic percentage of nitrogen after exposure. Further research and study will be required to

fully understand the effects of a nanoparticle coating on the UV-induced surface transformation to SiNCs.

REFERENCES

1. Zou, H.; Wu, S.S.; and Shen, J., *Polymer/silica nanocomposites: Preparation, characterization, properties, and applications*. Chemical Reviews, 2008. **108**(9): p. 3893-3957.
2. Balazs, A.C.; Emrick, T.; and Russell, T.P., *Nanoparticle polymer composites: Where two small worlds meet*. Science, 2006. **314**(5802): p. 1107-1110.
3. FDA, *Nanotechnology: A report of the U.S. Food and Drug Administration Nanotechnology Task Force*, in *Nanotechnology Task Force*. 2007, FDA.
4. EPA, *A Set of Scientific issues being considered by the EPA regarding: Evaluation of the hazard and exposure associated with nanosilver and other nanometal pesticide products*, in *FIRFA Scientific Advisory Panel*. 2010, EPA: Arlington.
5. Chin, J.; Byrd, E.; Embree, N.; Garver, J.; Dickens, B.; Finn, T.; and Martin, J., *Accelerated UV weathering device based on integrating sphere technology*. Review of Scientific Instruments, 2004. **75**(11): p. 4951-4959.
6. Nguyen, T.; Pellegrin, B.; Bernard, C.; Gu, X.; Gorham, J.M.; Stutzman, P.; Stanley, D.; Shapiro, A.; Byrd, E.; Hettenhouser, R.; and Chin, J., *Fate of nanoparticles during life cycle of polymer nanocomposites*. Journal of Physics: Conference Series, 2011. **304**: p. 012060.
7. Nguyen, T.; Pellegrin, B.; Bernard, C.; Rabb, S.; Stutzman, P.; Gorham, J.M.; Gu, X.; Yu, L.L.; and Chin, J.W., *Characterization of Surface Accumulation and Release of Nanosilica During Irradiation of Polymer Nanocomposites by Ultraviolet Light*. Journal of Nanoscience and Nanotechnology, 2012. **12**(8): p. 6202-6215.
8. Gorham, J.M.; Nguyen, T.; Bernard, C.; Stanley, D.; and Holbrook, R.D., *Photo-induced surface transformations of silica nanocomposites*. Surface and Interface Analysis, 2012. **44**(13): p. 1572-1581.
9. Gorham, J.M.; MacCuspie, R.I.; Klein, K.L.; Fairbrother, D.H.; and Holbrook, R.D., *UV-induced photochemical transformations of citrate-capped silver nanoparticle suspensions*. Journal of Nanoparticle Research, 2012. **14**(10).
10. Gorham, J.; Smith, B.; and Fairbrother, D.H., *Modification of alkanethiolate self-assembled monolayers by atomic hydrogen: Influence of alkyl chain length*. Journal of Physical Chemistry C, 2007. **111**(1): p. 374-382.